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Adsorbed State of Organic Compounds in Organo-Bentonite : II. Differential Thermal Analysis (Special Issue on Physical Chemistry)

AUTHOR(S):

Suito, Eiji; Arakawa, Masafumi; Yoshida, Tunoru

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Adsorbed State of Organic Compounds in Organo-Bentonite

II. Differential Thermal Analysis

Eiji SUIITO, Masafumi ARAKAWA and Tunoru YOSHIDA*

(Suito Laboratory)

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A study of molecular interaction between octadecylammonium ions and stearamide which were absorbed between the lattice layers of bentonite from aqueous solution has been undertaken by using the technique of differential thermal analysis.

The dissociation behavior of octadecylammonium and stearamide in bentonite complex at various mole ratios of octadecylammonium to stearamide provides evidence of the existence of the association complex of octadecylammonium and stearamide in the mole ratio of 1:1 between the lattice layers of bentonite.

INTRODUCTION

Numerous studies have been carried out on ion exchange adsorption and adsorption of polar molecule with bentonite and swelling of organic-bentonite complex in polar medium. With regard to the state of adsorbed molecules between the lattice layers of bentonite lamellae crystal, there is the study by Hoffmann¹⁾ *et al.* on ketone-bentonite. Adsorbed monolayer resembles the solid state rather than the liquid state and it is assumed that intermolecular interaction is larger than the interaction between organic molecule and internal surface of bentonite. Also, Farmer²⁾ *et al.* recently estimated the hydrogen bond between ethylammonium and ethylamine in the lattice layer of bentonite. The authors³⁾ previously reported on the interaction of octadecylammonium and stearamide in bentonite lattice layer using infrared spectrum. The strength of the interaction of ion and polar molecule in the internal surface of bentonite, together with the problem of its adsorption process is of considerable interest. From these points of view, a study was carried out on the adsorption state of organic species in octadecylammonium-stearamide complex bentonite, mainly by using differential thermal analyser. From the interpretation of the dissociation temperature and the peak area of adsorbed organic substances, it was inferred that the adsorbed state varied with the adsorbed mole ratio of ammonium ion and amide.

EXPERIMENTAL

1. Preparation of organic bentonite

The bentonite used was sodium bentonite produced in Gunma Prefecture.

* The paper in Japanese was reported in *Kogyo Kagaku Zasshi.*, **69**, 1125 (1966).

水渡英二, 荒川正文, 吉田 募

The acetic acid was added as the ionization reagent to a mixture of octadecylamine and stearamide, and heated at about 100°C. The mixture was added to bentonite solution of the same temperature and reacted by stirring. The mole ratio of amine to amide was changed from 3:1 to 1:3, and the total added quantity of both organic substances was such that it became 100 meq./100 g-clay for all mole ratios. The added quantity of organic substances was changed from 25 meq./100 g-clay to 200 meq./100 g-clay in case of octadecylammonium bentonite and octadecylammonium-stearamide bentonite whose mole ratios were the same. These reaction products were left standing over night. The precipitate was filtered and dried at 60°C.

Stearamide bentonite was prepared by dissolving stearamide in isopropanol and adding dry bentonite powder. This was dried at 105°C and then kept for 12 hours at room temperature under pressure of 4 mmHg.

Hereafter, octadecylammonium bentonite will be abbreviated as ODA-Bt, octadecylammonium-stearamide of equal mole ratio bentonite as (ODA+SA)-Bt, those with different mole ratios as (n ODA+ m SA)-Bt and stearamide bentonite as SA-Bt.

2. Experimental apparatus

The apparatus used were Model DT-2A differential thermal analyser and Model AX-2A X-ray diffractometer of Shimadzu Seisakusho Ltd.

3. Experimental procedure

The heating rate for the differential thermal analysis was 10°C/min. as a suitable size of peak can be obtained (range: $\pm 50, 100 \mu V$). The differential thermal analysis (DTA) mainly run in He or N₂ atmosphere.

Measurement of the area of DTA peak was made from the calibration curves obtained by mixing α -Al₂O₃ which was used as the standard with the sample in various ratios. As the deviation from linearity becomes great if the sample quantity exceeds 30 wt%, the range of mixing ratio was kept below this value. Correction for adsorbed water was made from the loss in weight when heated up to 200°C under the same condition. The method of Spiel-Ker⁴⁾ was used for obtaining the peak.

DTA measurements of the organic substances themselves were run without mixing with α -Al₂O₃.

RESULTS

1. Differential thermal analysis, X-ray diffractometry and thermogravimetric analysis

The relation of the DTA curve, the weight loss curve and the change in (001) reflection on heating are shown in Figs. 1 and 2. The endothermic peak which appears between about 300~400°C appears also in the measurement in He atmosphere. From these figures, it is clear that this peak is due to dissociation of adsorbed organic compounds.

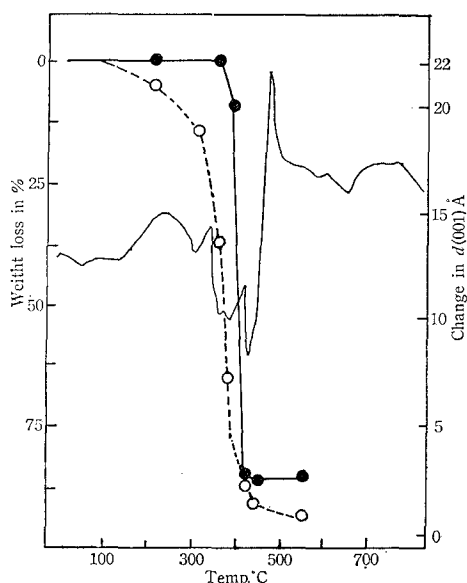


Fig. 1. Relation of DTA curve, weight loss curve and the change in $d(001)$ on heating, ((ODA+SA)-Bt, in air).

—●— $d(001)$ — DTA
 ...○... weight loss curve.

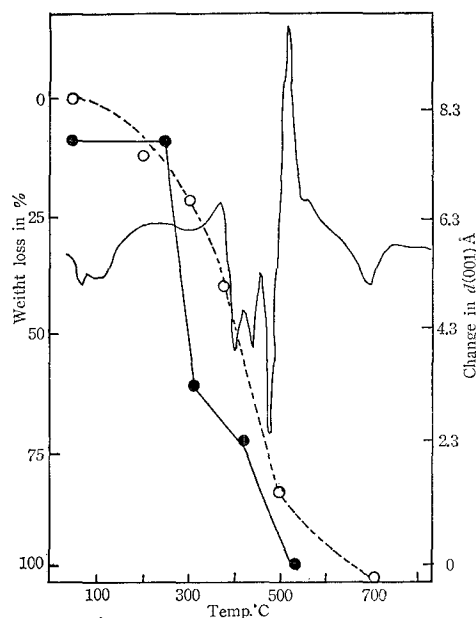


Fig. 2. Relation of DTA curve, weight loss curve and the change in $d(001)$ on heating, (ODA-Bt, in air).

—●— $d(001)$ — DTA
 ...○... weight loss curve.

2. X-ray diffraction

Fig. 3 shows the relation between $d(001)$ and composition of organic species in (n ODA+ m SA)-Bt. As shown in Fig. 4, the X-ray diffraction patterns of mixture of SA and bentonite change by heating (heated to 180°C) clearly. (A) indicates (001) reflection of bentonite, (B) and (C) are diffractions due to SA crystals.

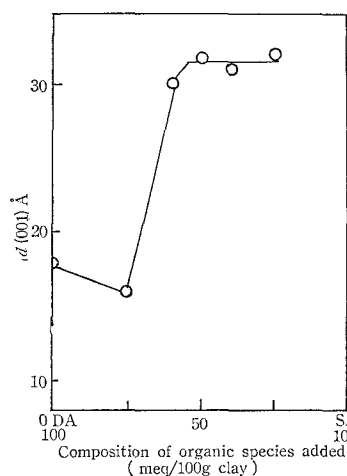


Fig. 3. Variation of (001) spacing of (n ODA+ m SA)-Bt with composition of organic species added.

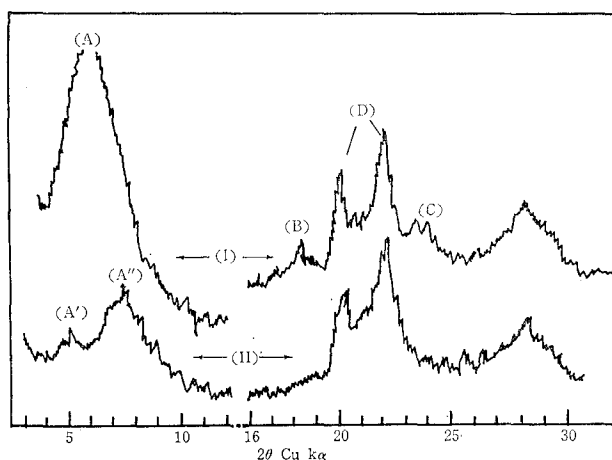


Fig. 4. Change in X-ray diffraction patterns for mixture of bentonite and SA on heating.

(I): before heating, (II): heated up to 180°C.

(A) separates into (A') and (A'') while (B) and (C) disappear on heating. (D) is the diffraction due to bentonite. The reduction from (A) to (A'') indicates the desorption of adsorbed water between the lattice layers of bentonite, and increase to (A') indicates that SA was adsorbed between the lattice layers. In case of SA-Bt, the same diffraction pattern is obtained but the intensity of (A') increases as the added quantity of SA is increased, as shown in Fig. 5. The same phenomenon was observed by Green-Kelly⁵⁾ on adsorbed pyridine.

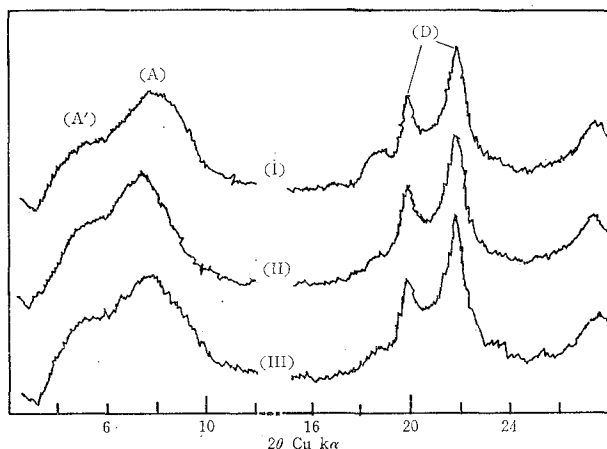


Fig. 5. Changes in X-ray diffraction patterns for SA-Bt with SA content.

(I) : 60 meq./100 g-clay, (II) : 80 meq./100 g-clay, (III) : 100 meq./100 g-clay.

3. Comparison of differential thermal analysis of organic substances and the organic bentonites

DTA curves of octadecylamine, air-dried emulsion of equi-moles of ODA and SA, and the organic bentonites are shown in Fig. 6. The endothermic peak at

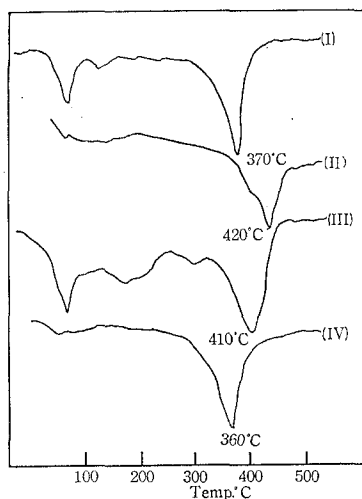


Fig. 6. DTA curves of organic bentonite and organic species, (in He).

(I) : ODA, (II) : ODA-Bt, (III) : ODA-SA emulsion (air dried),
(IV) : (ODA+SA)-Bt.

370°C of the curve of octadecylamine corresponds to its boiling point. The peak at 420°C of ODA-Bt is due to dissociation of ODA in the lattice layers of bentonite and its appearance at the higher temperature than the boiling point of octadecylamine indicates that ODA was adsorbed strongly in the layer by ion exchange.

In the case of (ODA+SA)-Bt, its endothermic peak appear at lower temperature than that of the air-dried emulsion of ODA-SA. The endothermic peak which

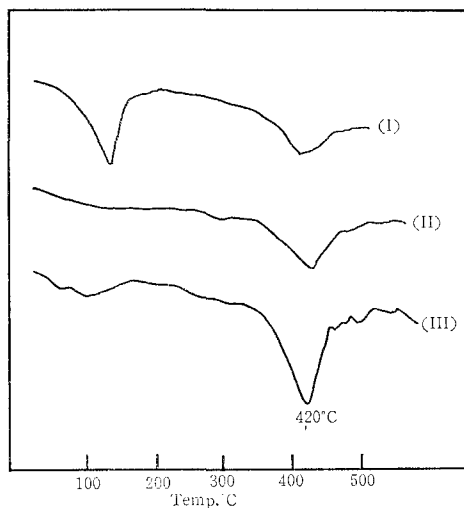


Fig. 7. DTA curves of ODA-Bt showing a change in peak size with ODA content, (in He).

- (I) : 25 meq./100 g.-clay,
- (II) : 50 meq./100 g.-clay,
- (III) : 100 meq./100 g.-clay.

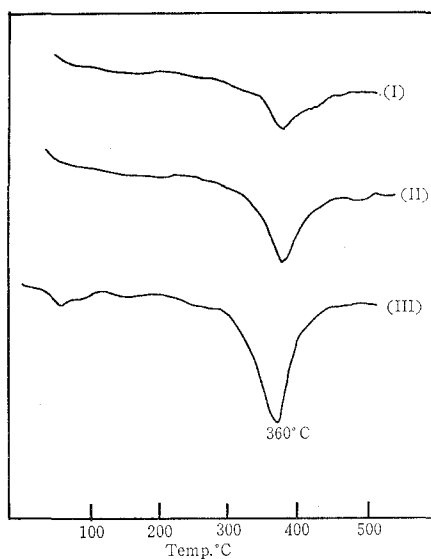


Fig. 8. DTA curves of (ODA+SA)-Bt showing a change in peak size with (ODA+SA) content, (in He).

- (I) : (25+25) meq./100 g.-clay,
- (II) : (50+50) meq./100 g.-clay,
- (III) : (80+80) meq./100 g.-clay.

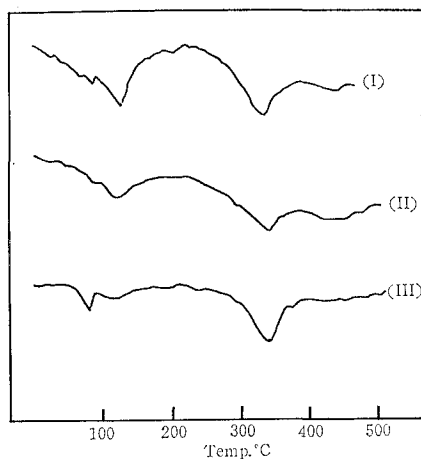


Fig. 9. DTA curves of SA-Bt and mixture of SA and bentonite, (in N₂).

- (I) : SA-Bt, 60 meq./100 g.-clay,
- (II) : SA-Bt, 40 meq./100 g.-clay,
- (III) : mixture of SA and bentonite.

appear at 60~100°C are due to the melting of octadecylamine and SA.

4. Variation of DTA curves with the amount of added organic compounds

Figs. 7 and 8 indicate variations of the peaks of ODA-Bt and (ODA+SA)-Bt with the added amount of organic compounds. There is no change in peak temperature, but there is variation in the size of the peak (the peak at about 120°C is due to dehydration of adsorbed water). Measurements were made with 30wt% of sample in case of ODA-Bt and 15 wt% in case of (ODA+SA)-Bt.

In case of SA-Bt, peak which assumed to be due to dissociation of SA appears at 330°C and a weak endothermic peak appears at about 450°C as shown in Fig. 9. In case of simple mixture of SA and bentonite, peak appears similarly at 330°C but the endotherm at about 450°C is not clear. The peak at about 80°C is due to the melting of SA.

5. Variation of DTA curves with mole ratio of ODA and SA in bentonite complexes

Fig. 10 shows the DTA curves of (n ODA+ m SA)-Bt when the mole ratios of ODA and SA, $n:m$, were changed. The total moles of ODA and SA in all cases were 100 meq./100 g-clay. When the content of ODA was in excess of SA, peak at 360°C and the shoulder at the higher temperature side appeared and the shoulder became smaller as the content of ODA decreased. If the contents of ODA and SA were the same, the strong peak at 360°C (see Fig. 8) became a single peak. When the content of SA became larger than that of ODA, a small peak appeared at 320~330°C and becomes larger as the content of SA increased.

It is clear that shoulder which appeared in excess content of ODA was due to ODA and the peaks which appeared at 360°C and 320~330°C were due to (ODA+

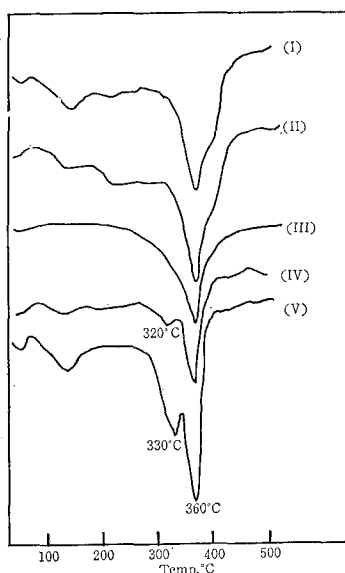


Fig. 10. DTA curves of (n ODA+ m SA)-Bt showing a change in peak with the mole ratio of ODA to SA, (in N_2).

(I): 3:1, (II): 3:2, (III): 1:1, (IV): 2:3, (V): 1:3.

SA) and SA, respectively. That is, the peak due to the dissociation of (ODA+SA) appeared over the entire range of ODA and SA mole ratio and when the content of either ODA or SA was larger, this peak appeared. Therefore, molecular association of ODA and SA in mole ratio of 1:1 in lattice layers of bentonite can be inferred.

6. Endothermic peak area

Fig. 11 shows the relation between endothermic peak area at 420°C of ODA-Bt and at 360°C of (ODA+SA)-Bt calculated from Figs. 7 and 8 respectively, and the amount of organic compounds. Similarly, Fig. 12 shows the relation between the total peak area of $(n\text{ODA}+m\text{SA})$ -Bt of Fig. 10, and the composition of organic species.

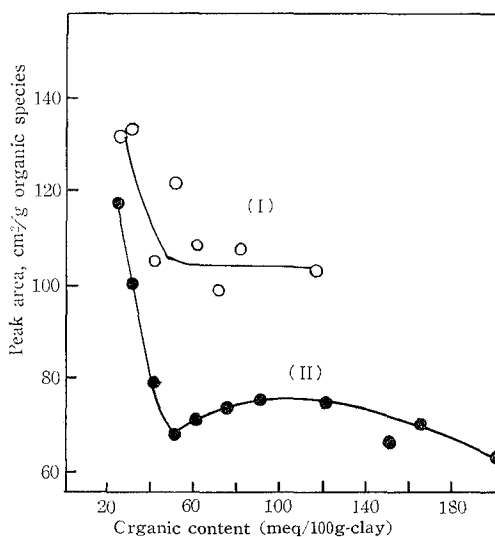


Fig. 11. Relation between the peak area and the amount of organic compounds.

(I): (ODA+SA)-Bt, (II): ODA-Bt

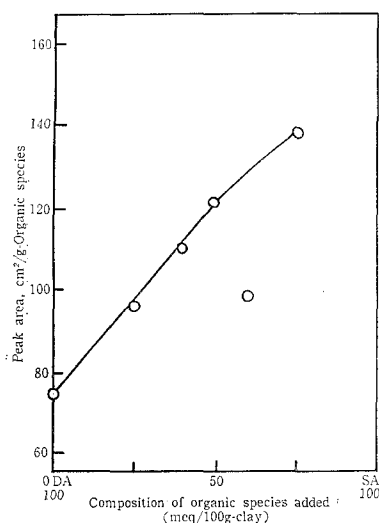


Fig. 12. Relation between the total peak area and the composition of added organic species for $(n\text{ODA}+m\text{SA})$ -Bt.

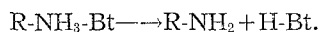
The deflection point at 50 meq./100 g-clay corresponds to the point at which monolayer of adsorbed ODA changes to two layerers^{3,6)} is clear in case of ODA-Bt but is not clear in case of (ODA+SA)-Bt. The peak areas of both curves were large when the organic content was small and became smaller gradually as the organic content increased. In case of $(n\text{ODA}+m\text{SA})$ -Bt, it increased approximately linearly with SA content.

DISCUSSION

The size of the alkyl group has a large influence on the adsorption of *n*-alkylammonium between the lattice layers of bentonite from aqueous solution. When the carbon number of alkyl group of amine is larger than 6, the amine is adsorbed in excess of the cation exchange capacity⁷⁾. Physical adsorption due to Van der Waal's force can take place easily as the molecule becomes larger

because the strength of Van der Waal's force depends on the relative size of the amine. On the other hand, when the alkylgroup of amine becomes larger the solubility of amine decreases. The organophilic property of internal surface of bentonite due to exchange adsorption increases. That is, the free energy of adsorption decreases as the alkyl group becomes larger.

It is believed that the peak area curve of ODA-Bt shows the heat of the reaction,



The point at 50 meq/100 g-clay in Fig. 11 is the point at which the two layers of ODA start to form and this is completed at 100 meq/100 g-clay³⁾. It is clear that the slight increase in peak area during this is due to the change in orientation of ODA and the difference in swelling energy of bentonite^{9,10,11)}. However, this is not clear in cases of (ODA+SA)-Bt and (nODA+mSA)-Bt.

The peaks at 330°C and 360°C of (nODA+mSA)-Bt when $m > n$ indicated in Fig. 10 and the shoulder at the higher temperature than 360°C when $m < n$ are due to dissociation of SA, (ODA+SA) and ODA, respectively, as is clear from Figs. 7, 8 and 9. It is clear that the difference in the peak area of (nODA+mSA)-Bt and the peak area of (ODA+SA)-Bt when $m = n$ corresponds to the excess

Table. I. Comparison of the peak area of (ODA+SA)-Bt with the divided peak area of (nODA+mSA)-Bt.

I	II	III	IV	V	VI
ODA : SA ($n : m$)	$\frac{\text{cm.}^2}{\text{g.}(n\text{ODA} + m\text{SA})}$	$\frac{\text{cm.}^2}{\text{g.}(\text{ODA} + \text{SA})}$	$\frac{\text{cm.}^2}{\text{g.ODA or SA}}$	ratio (calculated from II and III).	ratio (dividing the peaks).
25 : 75	139.1	131.1	146.9	0.54	
30 : 70	136.5	122.0	15.85	0.47	
40 : 60	130.0	112.0	200.0	0.32	0.33
50 : 50	121.8				
60 : 40	112.2	112.1	113.0	0.20	0.19
70 : 30	10.30	122.0	73.8	0.28	
75 : 25	96.2	131.1	61.2	0.31	0.4

(M+C+N) C' M or N

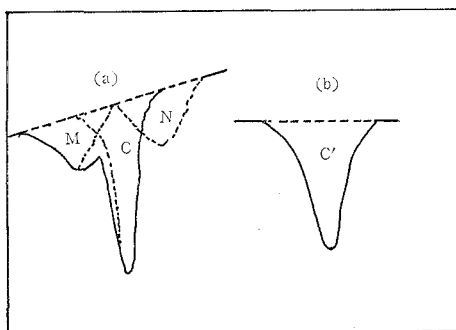


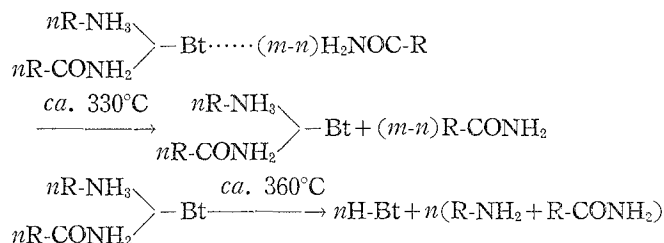
Fig. 13. Division of DTA peaks.
(a) : (nODA+mSA)-Bt, (b) : (ODA+SA)-Bt.

peak area of SA or ODA. The calculated results are shown in Table I. Column I shows the number of moles, n and m , in $(n\text{ODA}+m\text{SA})\text{-Bt}$ and column II the measured values of the peak area at that number of moles (see Fig. 13(a)). Column III shows the peak areas of $(\text{ODA}+\text{SA})\text{-Bt}$ which were obtained from the curve (I) in Fig. 11 (Fig. 13 (b)). The values of column IV are the peak areas corresponding to excess ODA or SA calculated from column II and column III. The values of column IV for $n>m$ are the peak areas due to ODA and show good agreement with the peak area of ODA-Bt obtained from the curve (II) in Fig. 11. Column V shows the ratios of peak area calculated from column II and column III to the total peak area and shows good agreement with the ratios obtained by dividing the peak of Fig. 4 shown in column IV. That is, the endothermic phenomenon at 360°C differs from that at 330°C or 420°C and is the same phenomenon as that at 360°C of $(\text{ODA}+\text{SA})\text{-Bt}$.

Strictly speaking, correction of the apparatus constants due to difference in reaction temperature is also necessary. However, when ODA and SA were adsorbed simultaneously, it is clear from Figs. 3 and 5, and also from the change in $d(001)$ of the previous report³⁾ that the adsorption of SA to internal surface of bentonite is accelerated much more by the adsorption of ODA.

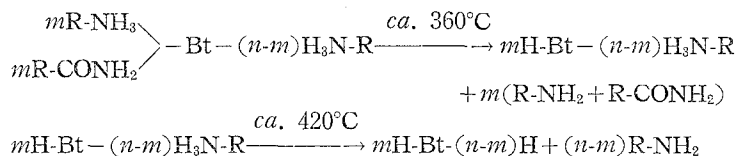
With regard to the dissociation temperature of ODA and SA from (n ODA + m SA)-Bt, it is considered as follows:

When $m > n$,



The excess SA dissociated at about 330°C and desorbed, but the complex (ODA+SA) remained in the internal surface of bentonite.

When $m < n$,



where H-Bt : hydrogen-bentonite

ODA which was adsorbed by ion exchange reaction dissociated at about 420°C.

It is concluded that the ODA and SA was associated with their active groups, -NH_3^+ and $\text{H}_2\text{NOC-}$, in a mole ratio of 1:1 in the internal surface of bentonite.

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